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(54) Title: POLYMERISATION REACTIONS UNDER MINIEMULSION CONDITIONS

(57) Abstract

A method of forming a polymer comprising: a) forming a miniemulsion including i) a monomer, ii) a non-aqueous solution including a cobalt-containing chain transfer agent, and iii) an aqueous solution; and b) reacting the miniemulsion in the presence of an initiator for a time sufficient to form the polymer.

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Polymerisation reactions under miniemulsion conditions

Technical Field

The present invention relates to a method for the formation of polymers by emulsion polymerisation and in particular to the formation of polymers under miniemulsion conditions.

Background Art

Emulsion polymerisation is widely used as a commercial process to produce a variety of latexes for a range of industries. Emulsion polymerisation processes are typically used to produce high molecular weight polymers, however, in recent times the advantage of generating much lower molecular weights for specific product applications has become evident. Catalytic chain transfer has been shown to be a highly effective synthetic tool for reducing molecular weight in free-radical solution/bulk polymerisation and emulsion polymerisation.

Limitations to the use of catalytic chain transfer agents in emulsion polymerisation reactions have been identified in the prior art. Firstly, such polymerisation reactions result in a loss of catalytic activity with time. This has, for example, been noted where cobaloximes are used as catalytic chain transfer agents. In addition, it has been noted that initiators which form oxygen centred peroxide radicals have a detrimental effect on the reaction, causing destruction of the catalyst. Similar behaviour has also been seen for oxygen centred persulfate radicals. This latter problem is highly inconvenient for commercial application of the technology, as persulfates are often the initiator of choice.

The present inventors have surprisingly found that one way of addressing the problem in the prior art is to separate the chain transfer agent from the primary initiator radicals by operating the chain transfer polymerisation reaction under miniemulsion conditions.

In miniemulsion polymerisation, the initial monomer droplet size, of about 100 nm is much smaller than conventional emulsion polymerisation, which is about 1 μm in size. Due to this size difference, particle nucleation occurs predominantly in the monomer droplets as opposed to creating a new particle phase.

Disclosure of Invention

In a first aspect, the present invention consists in a method of forming a polymer, the method comprising:

a) forming a miniemulsion including
   i) a monomer,
   ii) a non-aqueous solution including a cobalt-containing chain transfer agent, and
   iii) an aqueous solution; and

b) reacting the miniemulsion in the presence of an initiator for a time sufficient to form the polymer.

The initiator for the polymerisation reaction can be included in the reaction prior to the formation of the miniemulsion or in the miniemulsion.

A variety of monomers may be used in the present invention, including methacrylate derivatives, acrylate derivatives, acrylic acid, α-hydroxymethylacrylates, methacrylonitrile, α-hydroxymethylacrylonitrile, styrene and styrene derivatives. Methacrylate derivatives may be selected from, methyl methacrylate (MMA), ethyl methacrylate, *n*-butyl methacrylate, *i*-butyl methacrylate, benzyl methacrylate, methacrylic acid and 2-hydroxyethyl methacrylate. Preferably the styrene derivative is α-methyl styrene. It will be appreciated, however, that the present invention is not limited to these monomers.

A variety of cobalt-containing chain transfer agents with varying hydrophobicity may be employed in the present invention. Suitable chain transfer agents are ones that are able to partition equally between the oil and water phase or those that reside primarily in the oil phase. An example of a suitable cobalt-containing chain transfer agent able to reside equally between the oil and water phase is cobaloxime boron fluoride (COBF) (Figure 1). A suitable chain transfer agent able to reside exclusively in the oil phase is tetraphenyl cobaloxime boron fluoride (COPhBF) (Figure 1). Preferably, the catalyst is present in a concentration of between 1 to 25 ppm.

The aqueous solution may consist of a surfactant in deionised water. A variety of surfactants selected from anionic, cationic and non-ionic surfactants may be used in the present invention either singularly or in combination. Preferably, the surfactant is sodium dodecylsulfate (SDS).

An initiator is included in the reaction either prior to the formation of the miniemulsion or in the miniemulsion. A variety of initiators capable of

generating free radicals in an aqueous or organic phase may be used in the present invention. Suitable initiators include peroxides, persulfates, azo initiators and redox initiator systems. Preferable persulfate initiators include potassium persulfate (KPS), ammonium persulfate, sodium persulfate. Preferable azo initiators include azobisisobutyronitrile (AIBN), azobiscyanovaleric acid and azobis(2-amidinopropane)dihydrochloride (Vazo V50™). Preferable redox initiators include a redox couple from which each member is selected from iron catalysts, sodium metabisulfite and sodium formaldehyde sulfonate. Particularly preferred are initiators that generate oxygen centred radicals such as, persulfates and peroxides.

The concentration of the initiator used will depend on many variables including temperature, monomer and other reaction conditions. The appropriate concentrations to be used falls within the skill of a formulator of polymers.

AIBN produces carbon-centred radicals while KPS produces oxygen centred radicals. When AIBN is used as initiator, it is preferably added to the aqueous phase, prior to the formation of the miniemulsion, while KPS is preferably predissolved in water and added in the miniemulsion at the reaction temperature.

The emulsion may be stabilised by the presence of a highly water-insoluble compound (hydrophobe). A possible role of the hydrophobe is to minimise the Ostwald ripening effect (diffusion of the oil phase from small to large droplets to reduce the interfacial free energy of the system). The hydrophobe is preferably contained in the non-aqueous solution. The hydrophobe may be selected from a variety of alkanes and fatty alcohols, however, it will be appreciated that a suitable hydrophobe can be selected from a wide variety of other species. Preferably the alkane is hexadecane and the fatty alcohol is cetyl alcohol

An advantage of miniemulsion polymerisation is that highly water insoluble ingredients are present directly in the monomer droplets which are the locus of polymerisation, whereas in conventional emulsion polymerisation, monomer and other reaction components need to diffuse from the droplets via the water phase to the locus of the reaction (the particles). This can be exploited by dissolving highly water insoluble chain transfer agents directly into the monomer droplets, the loci of the reaction.

A miniemulsion can be formed in a variety of ways. Preferably it is formed from an emulsion by ultrasonification or high shear mixing at room temperature. In order to provide optimum polymerisation conditions, care should be taken at all steps to exclude oxygen from the system as the chain transfer agents are generally sensitive to oxygen once in solution. Typically, the cobalt-containing chain transfer agent is dissolved in the non-aqueous solution comprising the monomer which were preferably degassed by freeze-pump-thaw cycles, usually about three cycles. The monomer solution is transferred via a cannula to the aqueous solution, which has preferably been deoxygenated by purging with an inert gas, for example argon, for one hour, and initial emulsification is achieved using, for example, a magnetic stirrer. The miniemulsion may be generated by, for example, ultrasonification of the emulsion for approximately fifteen minutes using an ultrasonic bath.

Typically, reaction of the miniemulsion occurs in the same vessel in which the miniemulsion is formed.

The reactions may take place at any suitable temperature. A temperature range of about 40 to 80°C has been found to be particularly suitable. In a particularly preferred form, the reaction is controlled isothermally at about 65°C and ambient pressure in a flask fitted with a nitrogen purge and a magnetic stirrer. Samples may be removed periodically for conversion (by gravimetry) and molecular weight analyses. Typically, reaction times are two to four hours. It will be appreciated, however, that the reaction time will vary depending on the polymer being formed.

In a second aspect, the present invention consists in a polymer prepared by the method according to the first aspect of the present invention.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element or integer or group of elements or integers but not the exclusion of any other element or integer or group of elements or integers.

In order that the present invention may be more clearly understood, preferred forms will be described with reference to the following examples and accompanying drawings.

<u>Brief Description of the Figures</u>

Figure 1 shows structures of the chain transfer agents cobaloxime boron fluoride (COBF) and tetraphenyl cobaloxime boron fluoride (COPhBF).

Figure 2 is a graph showing dependence of M_n vs conversion on the concentration of catalyst (COBF and COPhBF) for AIBN initiated runs.

Figure 3 is a graph showing dependence of conversion vs time on the concentration of catalyst (COBF and COPhBF) for AIBN initiated runs.

Figure 4 is a graph showing dependence of M_n vs conversion on the concentration of catalyst (COBF and COPhBF) for KPS initiated runs.

Figure 5 is a graph showing dependence of conversion vs time on the concentration of catalyst (COBF and COPhBF) for KPS initiated runs.

Modes for Carrying Out the Invention

The following Examples further illustrate the present invention.

Six examples of miniemulsion polymerisation of methyl methacrylate using two different initiators (AIBN and KPS) and two different cobalt-containing chain transfer agents (COBF and COPhBF) have been described. The recipes for the miniemulsion polymerisation reactions carried out according to Examples 2 to 5 and 7 to 8 are outlined in Tables 1 and 2.

Table 1: Typical recipe for miniemulsion polymerisation reactions

Component	Mass/g
water	80
sodium dodecylsulfate	0.80
methyl methacrylate	20
hexadecane	0.50
initiator: AIBN or KPS	0.20
Catalyst: COBF or COPhBF	see Table 2

General procedure

Typically, the miniemulsion was formed by the following procedure. The surfactant, sodium dodecylsulfate (SDS), was dissolved in deionised water that was previously deoxygenated by purging with argon for one hour. The cobalt-containing chain transfer agent was dissolved in a non-aqueous solution comprising methyl methacrylate (MMA) and the hydrophobe (hexadecane), that were previously degassed by three freeze-pump-thaw cycles. The monomer solution was transferred via a cannula to the aqueous solution and initial emulsification was achieved using a magnetic stirrer.

The miniemulsion was generated by ultrasonification of the emulsion for fifteen minutes using an ultrasonic bath.

When AIBN was used as initiator, it was added to the aqueous phase with the SDS, prior to the formation of the emulsion. When KPS was used as the initiator, it was predissolved in water prior to the miniemulsion at room temperature.

All reactions were performed in batch. The reactions were controlled isothermally at 65°C in a flask fitted with a nitrogen purge and a magnetic stirrer. Samples were removed periodically for conversion (by gravimetry) and molecular weight analyses.

Molecular weight distributions may be measured by size exclusion chromatography (SEC) on a modular system, comprising an autoinjector, guard column, two mixed bed columns (60 cm mixed C and 30 cm mixed E, Polymer Laboratories) and a differential refractive index detector. The eluent may be tetrahydrofuran at 1 mL/min.

Final latex particle size distributions were measured using capillary hydrodynamic fractionation on a Matec Applied Sciences CHDF-1100 particle size analyser, calibrated with polystyrene latex standards.

Comparative Testing

In Examples 1 to 8, methyl methacrylate is polymerised under miniemulsion conditions in a series of experiments designed to show the advantages of cobalt-containing chain transfer agents in miniemulsion polymerisation. Miniemulsion polymerisation reactions with compositions as defined in Examples 2 to 5 and 7 to 8 (Tables 1 and 2) were compared with control polymerisation reactions containing no chain transfer agent, as seen in Examples 1 and 6. A summary of the runs conducted can be seen in Table 2.

Table 2: Summary of Runs

Examples	Run	Initiator	Catalyst	Concentration[a]
1	A1	AIBN	-	-
2	A2	AIBN	COBF	3.0
3	A3	AIBN	COBF	18
4	A4	AIBN	COPhBF	2.0
5	A5	AIBN	COPhBF	9.3
6	K1	KPS	-	-
7	K2	KPS	COBF	17
8	K3	KPS	COPhBF	2.0

[a] ppm mol/mol, equivalent to $[S]/[M] \times 10^6$, where [S] is the concentration of catalytic chain transfer agent and [M] is the monomer concentration.

Results from azobisisobutyronitrile (AIBN) Initiated Polymerisation

The influence of cobalt containing chain transfer agents on the miniemulsion polymerisation of MMA initiated by AIBN can be seen in Figures 2 and 3. The control polymerisation (run A1 with no chain transfer agent) produces a number average molecular weight, M_n, in the order of 10^6 which is typical of a miniemulsion polymerisation. Upon the addition of 3.0 and 18 ppm COBF the molecular weight of PMMA is drastically reduced to 87.0×10^3 and 4.41×10^3 respectively. A similar trend is noted for the COPhBF mediated reactions with an even greater reduction in molecular weight to 18.4×10^3 and 1.10×10^3 for a slightly lower concentrations of 2.0 and 9.3 ppm.

The first significant feature is that COPhBF appears to be a more effective catalyst than COBF under these conditions. This can easily be explained by the relative solubilities of the chain transfer agents in the two phases. It has been shown that COBF partitions approximately equally between the oil and water phase. Thus for the same overall catalyst concentration, the COBF concentration in the locus of polymerisation is less than the COPhBF concentration which resides exclusively in the oil phase.

Another important point to make is that all these reactions were performed in batch and in the case of COPhBF mediated polymerisation (run A4) the efficiency of the transfer process was maintained throughout the reaction to high conversion. This contrasts with previous emulsion studies

where the transfer efficiency rapidly waned, and effective molecular weight control could only be maintained by the steady feed of catalyst throughout the reaction. Clearly the present inventors have been successful in utilising miniemulsion polymerisation for effective compartmentalisation of the catalyst, preventing its contamination and degradation in the aqueous phase. Results of the reaction initiated with AIBN are given in Table 3.

Results from Potassium Persulfate (KPS) Initiated Polymerisation

The results for the KPS initiated polymerisation reactions of MMA are shown in Figures 4 and 5. The control polymerisation (K1), without a cobalt-containing chain transfer agent, produced very similar results to the corresponding AIBN run (A1) indicating no specific influence of initiator type on the reaction in the absence of cobalt containing chain transfer agents. Upon the addition of 3.0 ppm COPhBF the molecular weight is reduced from 900×10^3 to 17×10^3 which is comparable to the molecular weight reduction in the corresponding AIBN initiated reaction (run A4 where $M_n=18.4\times10^3$). This correlation shows that COPhBF maintains its efficiency as a chain transfer agent even in the presence of oxygen centred radicals. In the case of the COBF mediated reaction (K2) the molecular weight is reduced to 157×10^3 a much smaller effect than the corresponding AIBN initiated run (A3) which produced a molecular weight of 4.41×10^3 for similar catalyst concentrations. It is quite clear that in the case of COBF with KPS initiation there is a significant reduction in catalyst performance.

Table 3: Summary of final properties from each run

		Molecular weight Distribution Averages (MWD)			Particle size Distribution Averages (PSD)[a] (nm)			
Run	Conv[b]	M_n	M_w	PDi	D_n	D_w	PDi	N_c
A1	0.94	$828x10^3$	$2.12x10^6$	2.6	81	96	1.19	6.14
A2	0.65	$87.0x10^3$	$171x10^3$	20	96	135	1.41	3.69
A3	0.34	$4.14x10^3$	$10.8x10^3$	2.4	-	-	-	-
A4	0.92	$18.4x10^3$	$116x10^3$	6.3	85	125	4.47	5.23
A5	0.20	$1.10x10^3$	$3.76x10^3$	3.4	-	-	-	-
K1	0.99	$900x10^3$	$2.3x10^6$	2.6	77	86	1.12	7.15
K2	0.96	$157x10^3$	$436x10^3$	2.8	71	76	1.07	9.12
K3	0.93	$17.0x10^3$	$52.3x10^3$	3.1	77	84	1.09	7.15

a Omitted samples did not go to high enough conversion to be measured by CHDF

b Conversion of final sample taken

M_n Number average molecular weight

M_w Weight average molecular weight

PDi Polydispersity

D_n Number average diameter in nm

D_w Weight average diameter in nm

N_c Concentration of latex particles in L^{-1}

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Claims

1. A method of forming a polymer comprising:

a) forming a miniemulsion including

i) a monomer,

ii) a non-aqueous solution including a cobalt-containing chain transfer agent, and

iii) an aqueous solution; and

b) reacting the miniemulsion in the presence of an initiator for a time sufficient to form the polymer.

2. The method according to claim 1 wherein the monomer is selected from the group consisting methacrylate derivatives, acrylate derivatives, acrylic acid, α-hydroxymethylacrylates, methacrylonitrile, α-hydroxymethylacrylonitrile, styrene and styrene derivatives.

3. The method according to claim 2 wherein the methacrylate derivatives are selected from the group consisting of methyl methacrylate (MMA), ethyl methacrylate, *n*-butyl methacrylate, *i*-butyl methacrylate, benzyl methacrylate, methacrylic acid, and 2-hydroxyethyl methacrylate.

4. The method according to claim 2 wherein the styrene derivative is α-methyl styrene.

5. The method according to any one of claims 1 to 4 wherein the miniemulsion is stabilised by a hydrophobe.

6. The method according to claim 5 wherein the hydrophobe is included in the non-aqueous solution.

7. The method according to claim 5 or 6 wherein the hydrophobe is selected from alkanes and fatty alcohols.

8. The method according to claim 7 wherein the alkane is hexadecane and the fatty alcohol is cetyl alcohol.

9. The method according to any one of claims 1 to 8 wherein the cobalt-containing chain transfer agent partitions equally between the non-aqueous and aqueous solutions.

10. The method according to claim 9 wherein the cobalt-containing chain transfer agent is cobaloxime boron fluoride (COBF).

11. The method according to any one of claims 1 to 8 wherein the cobalt-containing chain transfer agent resides primarily in the non-aqueous solution.

12. The method according to claim 11 wherein the cobalt containing chain transfer agent is tetraphenyl cobaloxime boron fluoride (COPhBF).

13. The method according to any one of claims 1 or 12 wherein the initiator is included prior to formation of the miniemulsion.

14. The method according to any one of claims 1 or 12 wherein the initiator is included after formation of the miniemulsion.

15. The method according to any one of claims 1 or 14 wherein the initiator is selected from the group consisting of peroxides, persulfates, azo initiators, and redox initiators.

16. The method according to claims 15 wherein the persulfate initiator is selected from the group consisting of potassium persulfate (KPS), ammonium persulfate, and sodium persulfate.

17. The method according to claim 15 wherein the azo initiator is selected from the group consisting of azobisisobutyronitrile (AIBN), azobiscyanovaleric acid, and azobis(2-amidinopropane)dihydrochloride.

18. The method according to claim 15 wherein the redox initiator is selected from the group consisting of iron catalysts, sodium metabisulfate and sodium formaldehyde sulfonate.

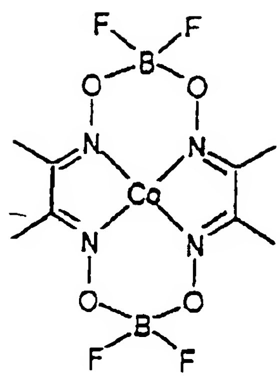
19. The method according to any one of claims 1 to 18 wherein the aqueous solution includes of one or more surfactants.

20. The method according to claim 19 wherein the surfactants are selected from the group consisting of anionic, cationic and non-ionic surfactants.

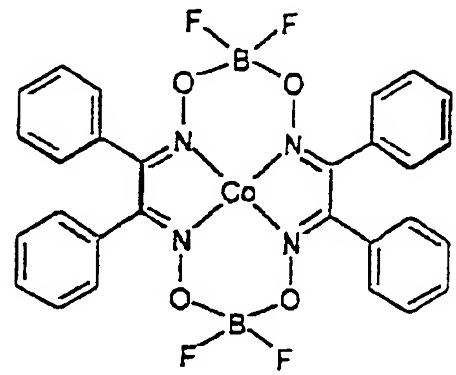
21. The method according to claim 20 wherein the surfactant is sodium dodecylsulfate (SDS).

22. The method according to any one of claims 1 or 21 wherein the reaction is controlled isothermally at 65°C and ambient pressure.

23. A polymer prepared by the method according to any one of claims 1 to 22.



cobaloxime boron fluoride
(COBF)



tetra phenyl cobaloxime boron fluoride
(COPhBF)

Figure 1

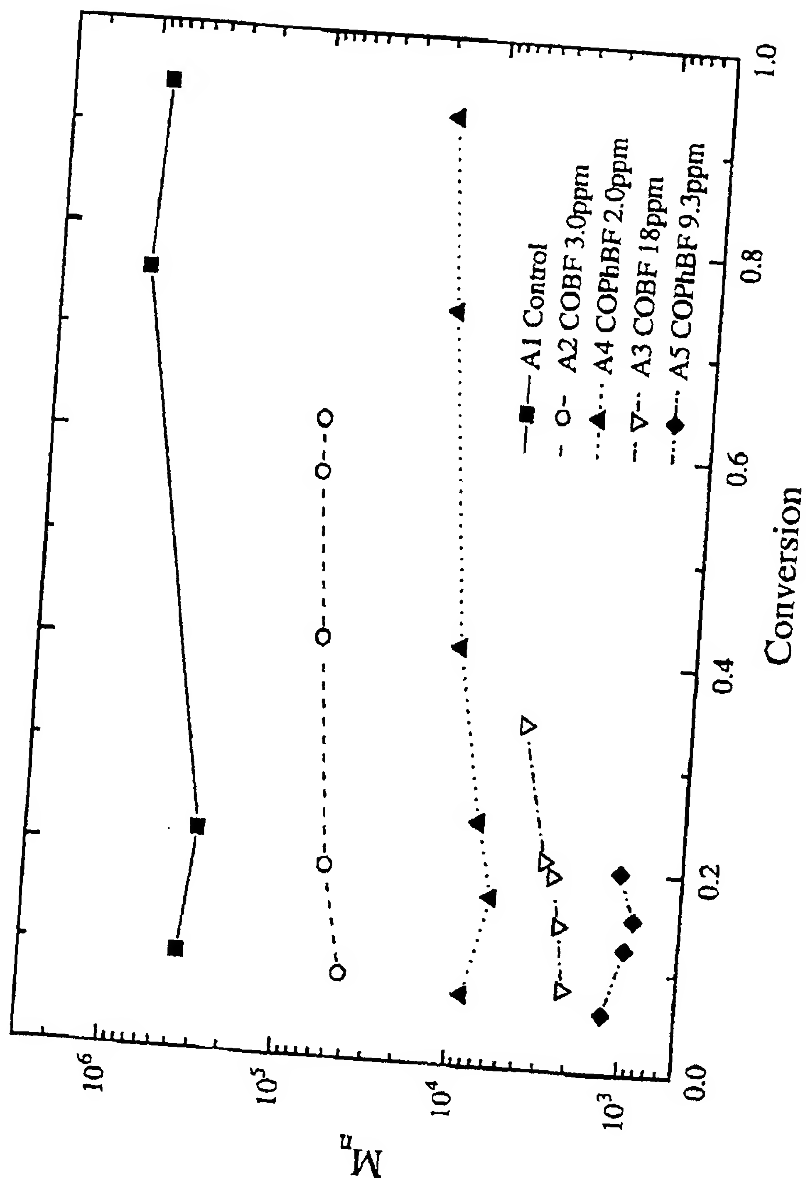

M_n
10^6
10^5
10^4
10^3
0.0
0.2
0.4
0.6
0.8
1.0
Conversion
A1 Control
A2 COBF 3.0ppm
A4 COPhBF 2.0ppm
A3 COBF 18ppm
A5 COPhBF 9.3ppm

Figure 2

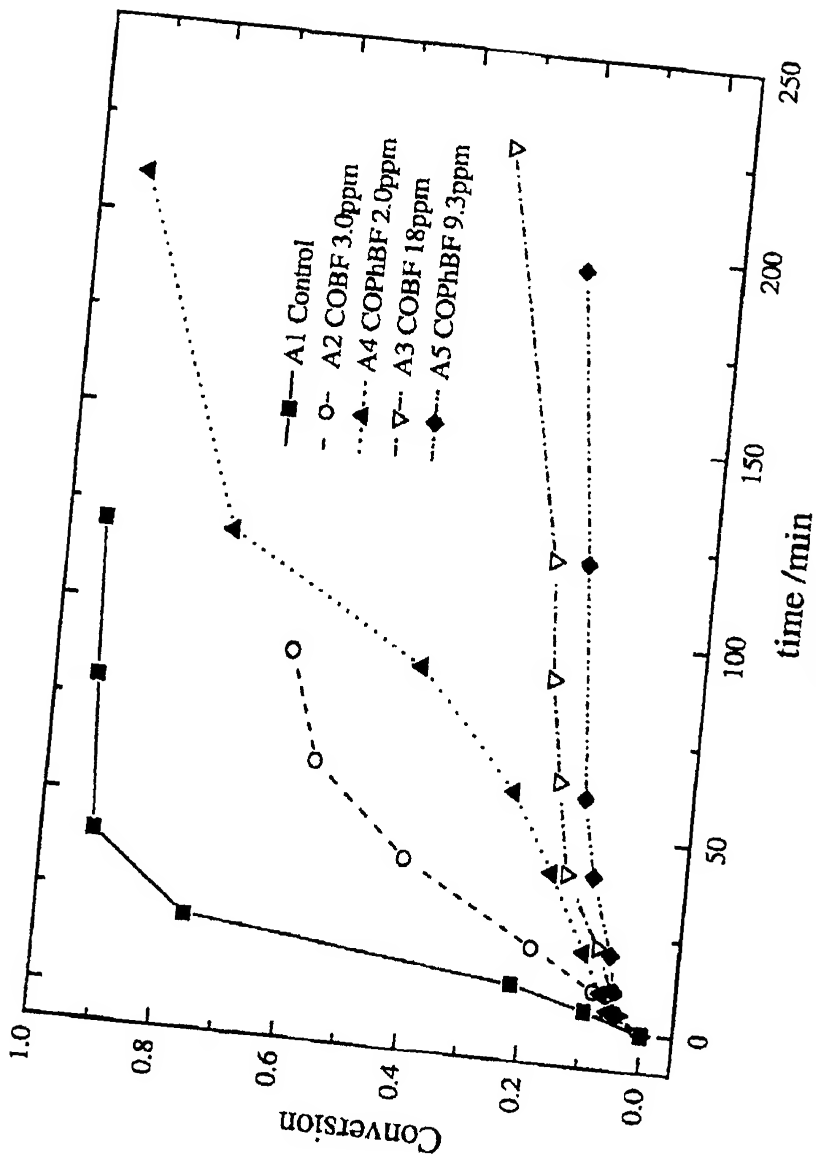

A1 Control
A2 COBF 3.0ppm
A4 COPhBF 2.0ppm
A3 COBF 18ppm
A5 COPhBF 9.3ppm
Conversion
0.0
0.2
0.4
0.6
0.8
1.0
0
50
100
150
200
250
time /min

Figure 3

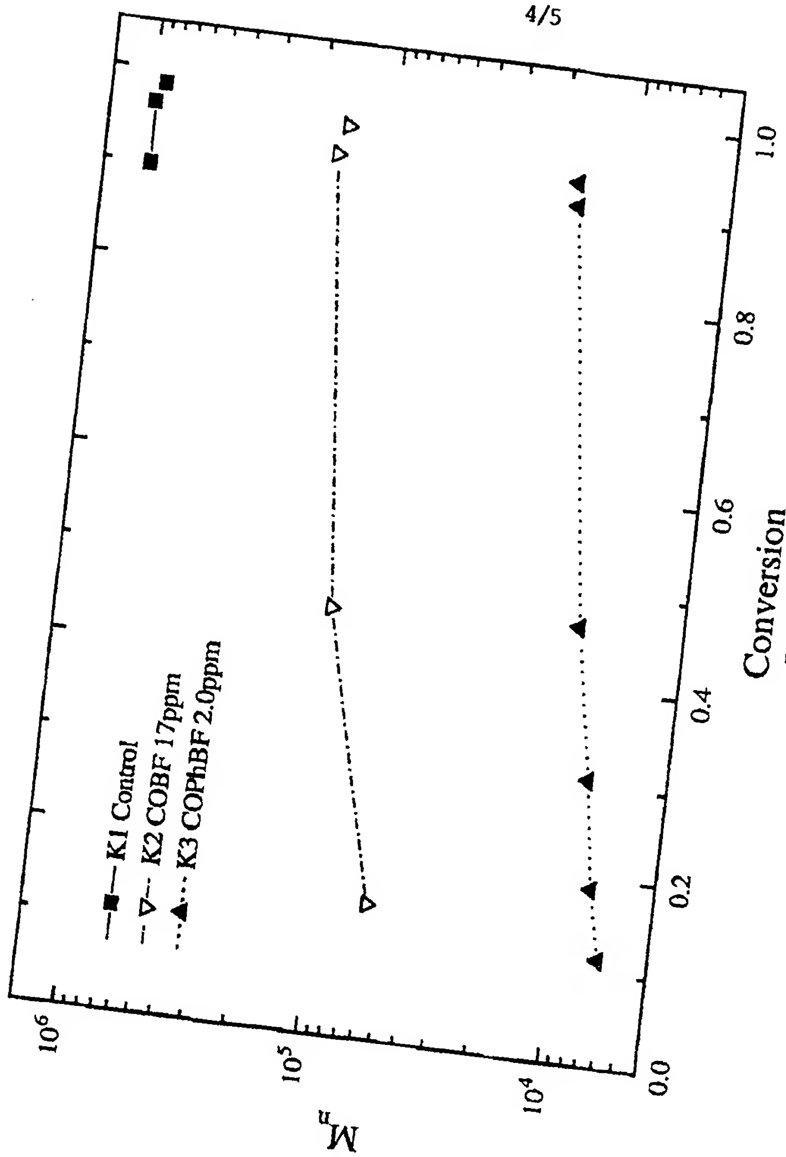

K1 Control
K2 COBF 17ppm
K3 COPhBF 2.0ppm
M_n
10^6
10^5
10^4
0.0
0.2
0.4
0.6
0.8
1.0
Conversion

Figure 4

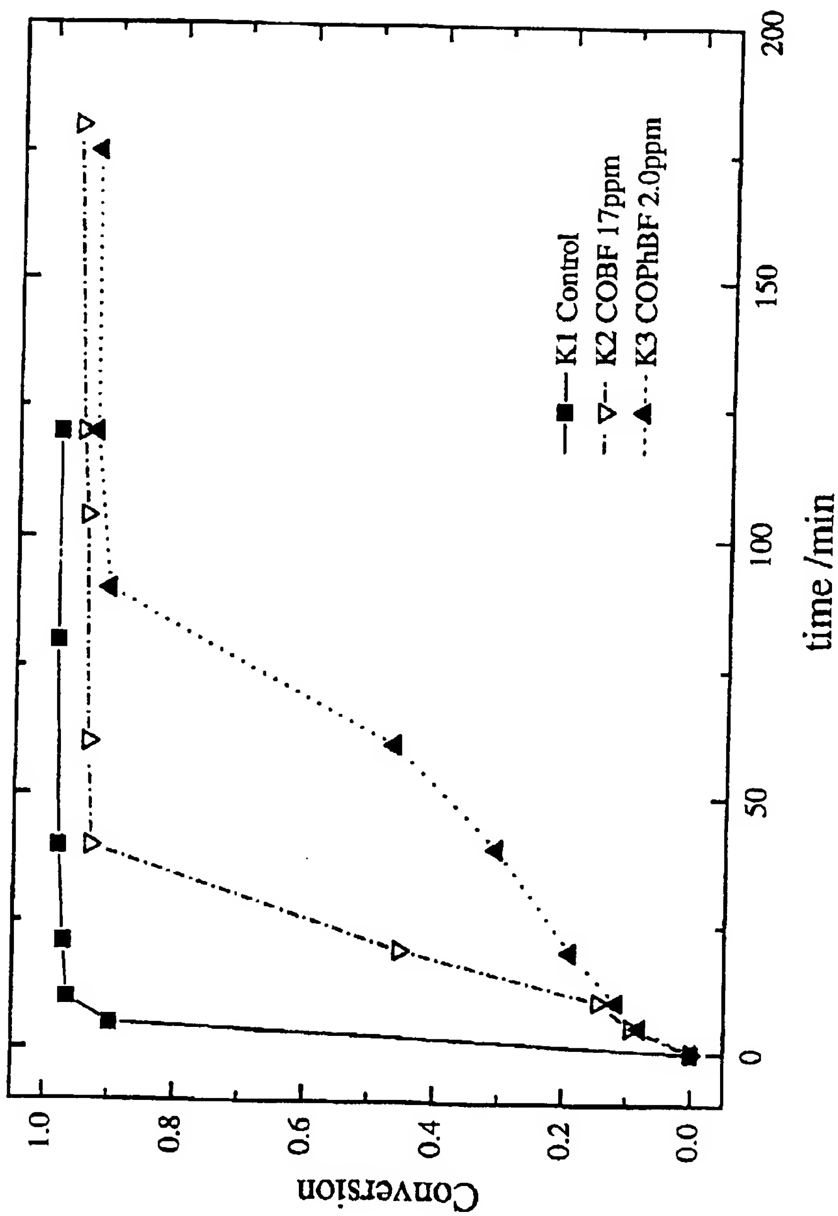

Conversion
0.0
0.2
0.4
0.6
0.8
1.0
0
50
100
150
200
time /min
K1 Control
K2 COBF 17ppm
K3 COPhBF 2.0ppm

Figure 5

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 98/00337

A.	**CLASSIFICATION OF SUBJECT MATTER**
Int Cl[6]:	C08F 2/38

According to International Patent Classification (IPC) or to both national classification and IPC

B.	**FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC C08F 2/38, 2/40, 2/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT: EMULSION POLYMER:

C.	**DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96/15158 A (E.I. DU PONT DE NEMOURS AND COMPANY et al.) 23 May 1996 whole document	1-23
A	EP, A, 199 436 (E.I. DU PONT DE NEMOURS AND COMPANY) 29 October 1986 whole document	1-23
A	US, A, 5 326 843 (ROHM & HAAS CO.) 5 July 1994 Abstract	1-23

☐ Further documents are listed in the continuation of Box C

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Date of the actual completion of the international search	Date of mailing of the international search report
12 June 1998	22 JUN 1998

Name and mailing address of the ISA/AU	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
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